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Effects of conditioners on sulfonamides degradation during the aerobic composting of animal manures

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Abstract

Sulfonamides (SAs) is one kind of the most important pharmaceuticals occurring in the environment. As the food additive, an increase application of SAs in the production of livestock and poultry leads to amounts of SAs excreted in manure, resulting in persistent environment pollution. Our research aimed to study the effects of some conditioners(sawdust, rice straw) on SAs degradation during the aerobic composting of animal manure. The experiments were conducted for 10 manure composting treatments as follow: hog manure,10 mg·kg⁻¹ SAs; hog manure+sawdust,10 mg·kg⁻¹ SAs; hog manure+rice straw,10 mg·kg⁻¹ SAs; hog manure,20 mg·kg⁻¹SAs; hog manure+sawdust,20 mg·kg⁻¹ SAs; hog manure+rice straw,20mg/kg SAs; Chicken manure,10 mg·kg⁻¹ SAs; Chicken manure+sawdust,10mg·kg⁻¹SAs; Chicken manure,20mg·kg⁻¹SAs; Chicken manure+sawdust, 20 mg·kg⁻¹SAs.The degradation of four SAs,sulfamerazine(SM1),sulfachlorpyridazine(SCP), sulfadimoxine(SDM'), Sulfaquinoxaline(SQ) were evaluated. The results showed that over 60% of 4 kinds of SAs were degraded in 35d of aerobic composting. Significant degradation of SM1, SCP, SDM', SQ were showed in treatments using conditioners than using manure alone. The reduction of 4 kinds of SAs ranged from 62.30 to 100% in all six treatments in aerobic composting, and the highest degraded rates were observed in six hog manure treatments with adding rice straws. It concluded that adding conditioners improved the degradation rate of 4 kinds of SAs during composting, which was considered as a practical and economical option for reducing antibiotic levels in animal manure before field use.

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Keywords: Animal manures; Sulfonamides; Composting; Conditioners; Degradation

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1. Introduction

Since their discovery in the early 1900s, antibiotics have been widely applied in treating infectious diseases which endanger humans and animals health seriously. With the fast development of livestock and poultry breeding, amount of antibiotics are used as food additive to improve animal growth [1-3]. More than 6 million kg of antibiotics are estimated to be used for veterinary purposes in the china, annually. The antibiotics in animal tissues are absorbed incompletely and parts of them are still excreted in urine and feces. Previous studies showed that high quantity of some antibiotics, as much as 70–90%, can be excreted as the parent compound in manures [2-3], and then storage in lagoons or pits during land application[4]. With respect to the manures kept in lagoons, the stationary phases of some infectious are up to 150 days [5]. Moreover, when antibiotics enter into soil with manure, they are relatively constant in 5–9 months [6,7]. Although their concentrations are very low, antibiotics still bring potential harms to human and animal in long-term exposure.

Composting is a controlled aerobic process, in which several kinds of microorganisms decompose organic materials and produce stable organic and inorganic byproducts [6-8]. Composting has been considered as an effective bioremediation strategy for soil, biosolids, and/or manure contaminated with explosives, aromatic and petroleum hydrocarbons [9], pesticides, personal care products [10], and hormones [11]. Previous studies of Dolliver[12], Bao[13], Arikan[14] showed that contents of tetracycline in manure could be reduced by composting. However, the variations of SAs during manure composting are still not clearly, and the depletion process of SAs is limited as well. Therefore, the objective of our study was to determine how these four kinds of SAs (sulfamerazine(SM1), sulfachlorpyridazine(SCP), sulfadimoxine(SDM'), Sulfaquinoxaline(SQ)) are degraded and what are their degradation rates in manure during composting.

2. Materials and Methods

2.1 Chemicals and standards

The Standard drugs(SM1, SCP, SDM', SQ) were obtained from Ehrenstorfer Company, with a Purity of over 98%. The drugs for composting were obtained from local veterinary drug store, with a purity of over 95%.

2.2 Experimental materials

In this experiment, two manure samples (chicken and hog manure) were collected from different livestock farms in Wenchang, Hainan province. Two kinds of SAs (SM1, SQ) residue were found in chicken manure samples, and the residual SM1 and SQ concentration in the manure samples were up to 19.38 and 120.33 $\mu\text{g}\cdot\text{kg}^{-1}$, respectively. There was no residual SAs in hog manure. In addition, the sawdust was obtained from a commercial sawmill, and rice straw was obtained from Agricultural planting. The main chemical properties of these different materials were shown in table1.

Table. 1. Physical and chemical properties of raw materials for composting

Material	C	N	C/N	Moisture content
Hog manure	15.32%	0.93%	16.47	53.6%
Sawdust	50.75%	0.84%	60.41	4.6%
Rice straw	40.18%	0.73%	55.04	10.2%

2.3 Equipment

There were 12 identical 100 L cylindrical plastic containers (0.8 m height×0.6 m in diameter) for the aerobic composting. At the bottom of each container, the ventilation tube was connected for aeration. Moreover, each container was covered by 100mm crushed stone. Time controller and valve were used to control ventilation rate and time. The equipment for composting was shown in Fig 1.

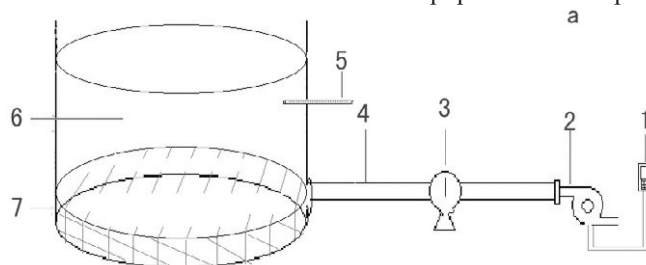


Fig. 1. The equipment for aerobic composting;

(1) time controller; (2) blower; (3) flowmeter; (4) Ventilation pipe; (5) thermometer; (6) compost material; (7) Aerated layer; (8) discharge port; (9) black Plastic film; (10) air-vent

2.4 Composting experimental design

Ten manure composting treatments were shown as follows: Chicken manure, 10mg·kg⁻¹ SAs(T1); Chicken manure+sawdust, 10mg·kg⁻¹ SAs(T2); Chicken manure, 20mg·kg⁻¹ SAs(T3); Chicken manure+sawdust, 20mg·kg⁻¹ SAs(T4); hog manure, 10mg·kg⁻¹ SAs(T5); hog manure+sawdust, 10mg·kg⁻¹ SAs(T6); hog manure+rice straw, 10mg·kg⁻¹ SAs(T7); hog manure, 20mg·kg⁻¹ SAs(T8); hog manure+sawdust, 20mg·kg⁻¹ SAs(T9); hog manure+ rice straw, 20mg/kg SAs(T10); 10 composting bins were filled with 50 kg mixture in each one, and then compacted.

In this experiment, the moisture contents were kept at 65% material capacity water. The initial C: N ratio was adjusted to 25 by adding sawdust or rice straw. The rice straw was cut in 5 cm long pieces. Four SAs were added and mixed with manure and other materials at target concentrations of 10 and 20 mg·kg⁻¹. All samples were thoroughly mixed manually in a plastic tray.

The composting samples were aerated for every 4 hours, and the Ventilation rate was set to 0.050 m³·min⁻¹ in first two weeks but 0.030 m³·min⁻¹ in last four weeks. Samples for analysis were taken from each manure composting test at days 0, 7, 14, 21, 28 and 35 of composting for determination of 4 SAs concentrations and moisture content of the composting samples. 10 samples were taken from each container, mixed thoroughly, and a composite sample was collected in a plastic bag. Samples were collected at 7 day intervals. The samples were immediately brought to the laboratory and analyzed for their antibiotic content. The samples were then stored at 4°C to determine other parameters (N, pH, total P and K). All analyses were completed within one week of sampling. Temperature was measured daily by a digital thermometer in the centre of the material.

2.5 Antibiotic Analysis

Contents of 4 sulfonamides (SM1, SCP, SDM', SQ) residues in composting samples were analyzed by high performance liquid chromatography (HPLC) with fluorescence detection detector. The samples were

extracted with 25mL methanol for three times, and then the combined extracts were evaporated to dryness under reduced pressure at 45 °C. The residue was dissolved in 0.1 mol•L⁻¹ HCl and the analytes were derived with fluorecamine. The chromatographic separation was performed on a C18 column with a gradient elution program using mobile phases based on mixtures of acetonitrile: 0.5% acetic acid aqueous =40:60 solution. The four sulfonamides were separated within 20 min.

3. Results

3.1 Composting process for aerobic composting

The odor of 10 treatments was stronger with adding the mixture of antibiotic and water, and then it became smaller after 4d, even disappeared after 15d. Significant differences in temperature of composting were observed in all 6 treatments. Over 60°C temperature in 3d was found in all 10 treatments, and then 54~64 °C temperature was kept in five consecutive days. Subsequently, the temperature decreased to 42~49°C in 13 days. With adding mixing water again in 14 d, all 10 treatments kept temperature at 48 ~62°C, and then its decreased again at the same as external temperature.

3.2 Degradation of 4 SAs

Degradation of 4 SAs during composting

Previous studies showed that tetracycline in manure could be degraded by composting. Our results (Table 2) showed that all treatments of composting can definitely reduce contents of SAs. In this study, the high level treatment had the similar degradation trend for 4 SAs as the low level treatment, 35 d of thermophilic composting resulted in >82.05% reduction in SM1, >79.48% reduction in SCP, >88.95% reduction in SDM', >62.23% reduction in SQ.

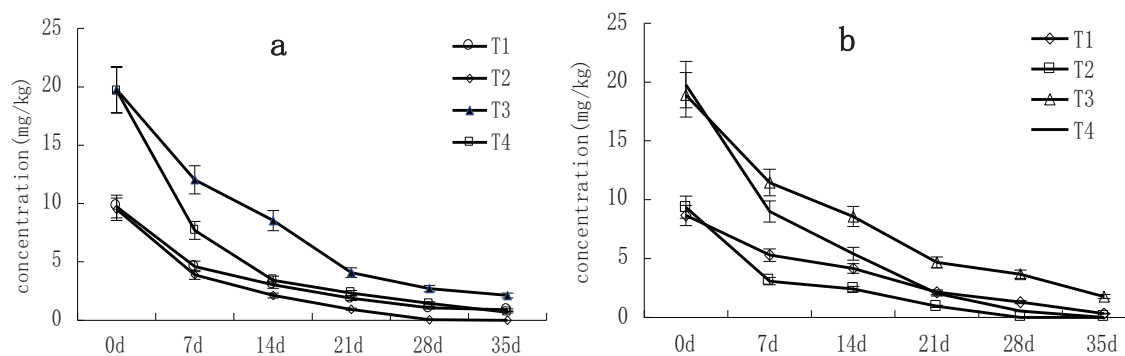
Table .2. Percentage of 4 SAs reduction in different treatments of composting after 35d

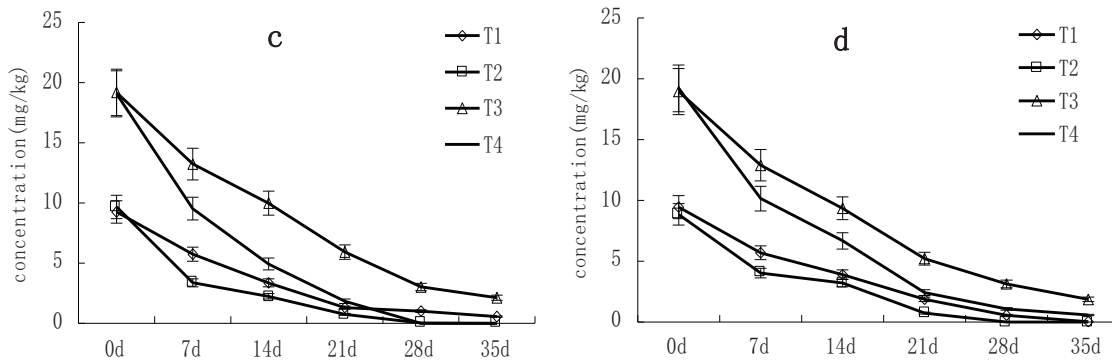
Composting treatments	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
SM ₁	90.97	100	88.95	96.55	83.61	99.78	100	82.05	93.15	100
SCP	96.30	100	90.69	100	100	99.67	100	79.18	96.82	100
SDM'	99.40	100	88.95	100	97.73	100	100	94.60	100	100
SQ	99.68	100	90.20	96.98	89.56	100	100	62.23	98.45	94.70

The effect of 4 SAs Degradation by adding materials during composting

Our results showed that the addition of sawdust or rice straw were more useful for the degradation of 4 SAs in low or high level treatments than adding nothing except the drugs. The variations of extractable (a) SM1, (b) SCP, (c) SDM', (d) SQ during composting of chicken manure were observed in Fig 2. In this study, two level treatments were designed. The SAs removals were investigated in different composting phases. During the 0-7 d heating phase of T1, T2 treatments, the SM1 removal were 52.77% and 59.10%, SCP were 38.91% and 67.20%, SDM' were 38.01% and 65.15%, SQ were 39.85% and 53.85%, the total removal percentages of SM1 in the 0-35 d were 90.97% and 100%, SCP were 96.30% and 100%, SDM' were 99.40% and 100%, SQ were 99.68% and 100%. During T3, T4 treatments in the 0-7 d heating phase, the SM1 removal percentages were 39.10% and 60.91%, SCP were 39.42% and 54.50%, SDM' were 31.02% and 50.08%, SQ were 32.01% and 47.14%, the total removal percentages of SM1 in the 0-35 d were 88.95% and 96.55, SCP were 90.69% and 100%, SDM' were 88.95% and 100%, SQ were 90.20% and 96.98%.

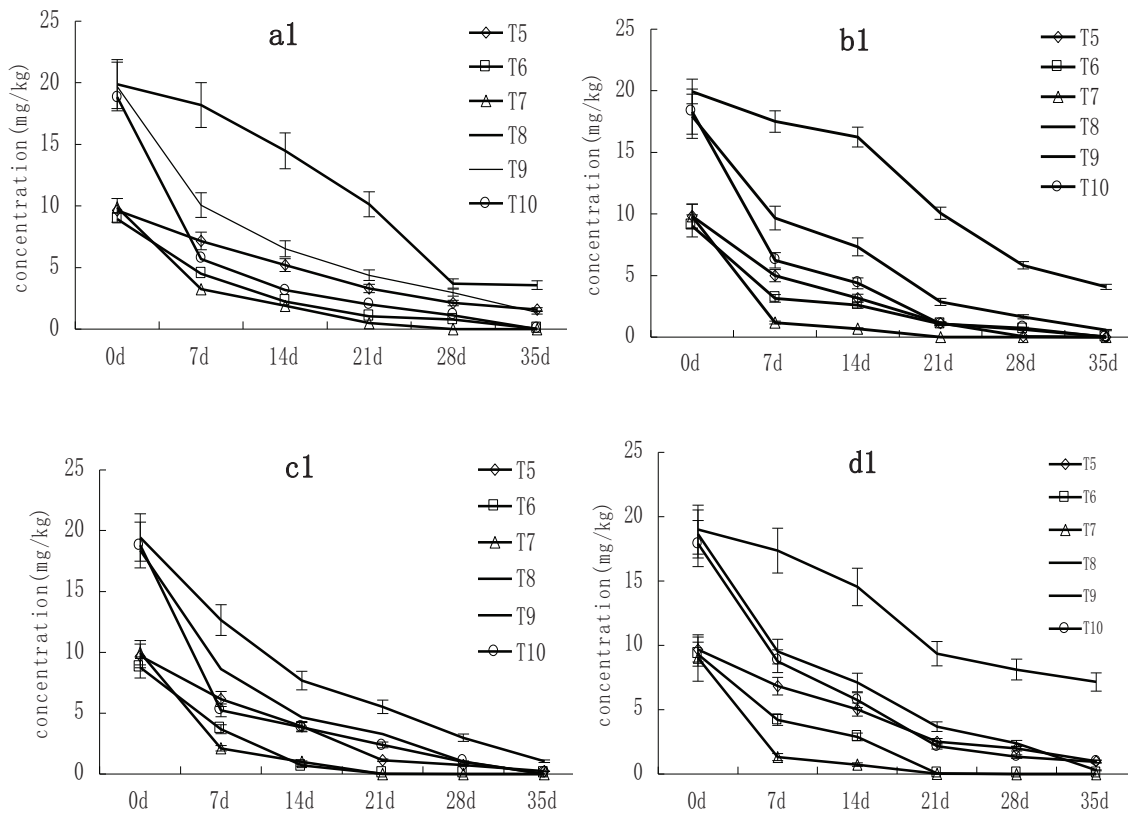
The variations of SAs concentration in composting of hog manure were similar as the composting of chicken manure (Fig 3). During the 0-7 d heating phase of T5, T6 and T7 treatments, the SM1 removal percentages were 25.73%, 49.56% and 67.21%, SCP were 49.19%, 65.23% and 87.96%, SDM' were 35.56%, 60.00% and 78.84%, SQ were 29.37%, 54.89% and 85.27%, the total removal percentage of SM1 in the 0-35 d were 83.61, 99.78 and 100%, SCP were 100, 99.67 and 100%, SDM' were 97.73, 100 and 100%, SQ were 89.56, 100 and 100%. During the 0-7 d heating phase of T8, T9 and T10 treatments, the SM1 removal percentages were 8.50%, 48.89% and 69.80%, SCP were 12.20%, 46.04% and 65.90%, SDM' were 34.88%, 53.10% and 72.20%, SQ were 8.58%, 48.95% and 51.03%. With the different thermophilic composting conditions, 4 SAs were degraded, the total removal percentages of SM1 in the 0-35 d were 82.05, 93.15 and 100%, SCP were 79.18, 96.82 and 100%, SDM' were 94.60, 100 and 100%, SQ were 62.23, 98.45 and 94.70%. The results above indicated that the degradation of 4 SAs using manure+ sawdust or manure+ rice straw was more effective than treatments using mature alone. During composting of hog manure, adding rice straw in composting bins was the most effective in all six treatments.





(T1):Chicken manure,10mg·kg⁻¹SAs; (T2):Chicken manure+sawdust,10mg·kg⁻¹SAs;
 (T3):Chicken manure,20mg·kg⁻¹SAs; (T4):Chicken manure+sawdust,20 mg·kg⁻¹SAs;

Fig. 2. Variations of extractable (a) SM₁, (b) SCP, (c) SDM', (d) SQ during composting of chicken manure



(T5): hog manure, 10 mg·kg⁻¹SAs; (T6): hog manure+ sawdust, 10 mg·kg⁻¹ SAs;(T7): hog manure+ rice straw, 10 mg·kg⁻¹SAs; (T8): hog manure, 20mg·kg⁻¹SAs; (T9): hog manure+ sawdust, 20mg·kg⁻¹SAs; (T10): hog manure+ rice straw, 20mg/kg SAs;

Fig. 3. Variations of extractable (a1) SM₁,(b1) SCP,(c1) SDM',(d1) SQ during composting of hog manure

4. Discussion

Composting has been considered as a feasible method for antibiotics degradation in manure, but studies is still limited. The mechanisms of degradation in compost is generally correlated to soil or other matter (manure, biosolids, sediments, etc.) degradations similar [15]. Brij Verma et al [16] indicated that a half-life of antibiotics could decrease due to microbial frequent activities. Flemming Ingersl et al [17] found that the temperature increase was helpful to degrade antibiotics. Moreover, other studies confirmed the abiotic degradation of tetracycline and proposed the abiotic processes during composting and stockpiling might be one of reasons for chlortetracycline degradation [18]. In our study, all of four SAs were degraded during thermophilic composting process, which might be correlated with the activities of microbial, the increase of temperature and other factors.

Conditioners are important assistant materials in the composting process. The former researcher found that adding conditioners on composting process was necessary for adjusting the (C/N) ratio of the materials, regulating moisture content, modulating the free air space, reducing the odors, improving nutrient contents and promoting the growth of microorganisms. In our study, the degradation of 4 SAs using manure+ sawdust or manure+ rice straw was more effective than other treatments using mature alone, which might reflect the higher activities of microorganism in the former. In addition, most effective degradation in treatments with rice straw additions may be attributed to the larger volume of rice straw easily to be biodegraded in the composting.

5. Conclusions

Composting can effectively promote the depletion of CTC whether in hog manure or chicken manure. In this study, over 60% degradation of 4 kinds of SAs was observed in 35 d of aerobic composting. The degradation rates of 4 SAs in treatments using manure+ sawdust or manure+ rice straw was much more effective than other treatments using mature alone. Moreover, adding rice straw was the most effective method for SAs degradation in six hog manure treatments. So far, it is still lack of studies about the depletion of SAs in composting, more experiments are needed to determine the degradation of different antibiotic compounds in other manure types and management systems.

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